

## PATENT ABSTRACTS OF JAPAN

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TSUCHIDA HIDEKI

## (54) HEAT-SENSITIVE RECORDING BODY

## (57)Abstract:

PROBLEM TO BE SOLVED: To prevent wetting blocking or the like problem, by forming a protecting layer by using silicon modified polyvinyl alcohol and also glyoxal and epichlorohydrin as a hardener in a heat-sensitive recording body having a heat-sensitive coloring layer and the protecting layer set on a supporting body.

SOLUTION: A heat-sensitive recording body which can record images according to a heat-sensitive recording method has a heat-sensitive coloring layer and a protecting layer set on a supporting body. The protecting layer is formed with the use of silicon modified polyvinyl alcohol and also glyoxal and epichlorohydrin as a hardener. The silicon modified polyvinyl alcohol used is polyvinyl alcohol including silicon in molecules which is produced by introducing silicon into polyvinyl alcohol or polyvinyl acetate with the use of a silylating agent, i.e., by a post modification method or the like. A compounding amount of glyoxal as the hardener is 10-30 pts.wt. based on 100 pts.wt. of silicon modified polyvinyl alcohol.

## LEGAL STATUS

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CLAIMS

[Claim(s)]

[Claim 1] The thermal recording object characterized by this protective layer using glyoxal and epichlorohydrin together as a curing agent further using silicon denaturation polyvinyl alcohol in the thermal recording object which has a base material, the sensible-heat coloring layer formed on this base material, and the protective layer formed on this sensible-heat coloring layer.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to amelioration of the \*\*\*\*\* blocking property of a protective layer established on the heat-sensitive recording layer in more detail about the thermal recording object which can record an image by thermal recording, a wet love property, and the stability of a protective layer coating.

[0002]

[Description of the Prior Art] By having the sensible-heat coloring layer formed on the base material generally, and heating a sensible-heat coloring layer with a heat head, a heat stylus, laser light, etc., a thermal recording object makes the color coupler in a sensible-heat coloring layer react in an instant, forms a record image, and is widely known by JP,43-4160,B, JP,45-14039,B, etc. from the former.

[0003] These thermal recording objects can form a record image with comparatively easy equipment, and since they moreover have an advantage, like a maintenance is easy and there is also little noise at the time of record, they are applied, for example to wide range fields, such as printers for terminals, such as a recorder for measurement, facsimile, and a computer, a printer for POS, an automatic ticket vending machine, and a bar code Label Printer. the application of a thermal recording object is expanded to the various objects for tickets, the object for receipts, the object for ATM of a bank, gas, the object for the electric inspection of a meter, etc., and problematic [ to a thermal recording object / in the former ] in especially recent years, for this reason — \*\*\*\* — a severe property which was not is beginning to be required. That is, moreover, the property required of a thermal recording object may be used outdoors by rainy weather in the applications gas, for the electric inspection of a meter, etc. with weatherability, chemical resistance, etc. not to mention having the resistance over that a record image fades, a natural complexion fogging, etc., and the resistance over water is also required.

[0004] On the other hand, the conventional thermal recording ingredient has the fault which a record image fades or the natural complexion section colors by contacting organic solvents, such as fats and oils, such as plasticizers and salad oil, such as phthalic-acid diester represented by the dibutyl phthalate ester contained in a vinyl chloride case, and an aliphatic series dibasic acid ester, trialkyl phosphate, and a hand cream, or ethyl alcohol, and toluene, etc. In order to conquer such a fault, preparing a protective layer on a sensible-heat coloring layer from the former is performed, and water soluble polymers, such as polyvinyl alcohol and starch, etc. are used as a principal component as a component which constitutes this protective layer.

[0005] For this reason, when using the thermal recording object which moreover has a protective layer by rainy weather outdoors, if it contacts immediately after the thermal recording objects after record are damp in water, a thermal recording side, its rear face, or thermal recording sides will paste up. Fault, such as producing blocking and producing the poor feeding of the recording paper as a result, when a thermographic recording paper exfoliates and produces the problem that the recorded information cannot be read from paper, in being the worst, the end and, or waterdrop falls to the side face of winding before record and a sensible-heat side and its rear face paste up with waterdrop, has occurred.

[0006] Using together such a water soluble polymer and the cross linking agent which reacts as an approach of making it giving a water resisting property to the protective layer of a thermal recording object to solve this is performed. However, when heat energy which produces crosslinking reaction sufficient in the case of formation of a protective layer not being made giving, and a reactant high cross linking agent are used, crosslinking reaction arises in coating liquid, the viscosity of coating liquid increases remarkably, and there is a problem of coating becoming impossible etc.

[0007] In order to solve such a problem, introducing the functional group which raises reactivity to a water soluble polymer is proposed. For example, although the proposal of JP,56-126193,A, JP,59-106995,A, JP,59-169885,A, JP,62-264990,A, etc. is made, even if it uses these denaturation poly vinyl, the \*\*\*\*\* blocking property is inadequate.

[0008] Although it is a technique well-known at JP,58-193189,A to use silicon denaturation polyvinyl alcohol for a protective layer, if it uses independently, a water resisting property cannot be given. In order to compensate these faults, using glyoxal for silicon denaturation polyvinyl alcohol is indicated by JP,04-232091,A and JP,05-185718,A. However, in a glyoxal independent, the stability of a coating is low and a technical problem remains also in a wet love property. Furthermore, although mixing chitosan and glyoxal to silicon denaturation polyvinyl alcohol in JP,8-183252,A at a protective layer is proposed, this proposal also has the low stability of a coating and has the fault of being easy to yellow the acquired thermal recording object.

[0009]

[Problem(s) to be Solved by the Invention] Even if the coating stability of this invention of a protective layer is high and it uses it in respect of quality on the outdoors of rainy weather, problems, such as \*\*\*\*\* blocking, do not arise, and it aims at offering the thermal recording object excellent in the water resisting property.

[0010]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, this invention adopts the following configurations. That is, this invention is a thermal recording object characterized by this protective layer using glyoxal and epichlorohydrin together as a curing agent further using silicon denaturation polyvinyl alcohol in the thermal recording object which has a base material, the sensible-heat coloring layer formed on this base material, and the protective layer formed on this sensible-heat coloring layer.

[0011]

[Embodiment of the Invention] If the silicon denaturation polyvinyl alcohol used for this invention is polyvinyl alcohol which contains

silicon in intramolecular, it is good anything. As the manufacture approach, the approach indicated by JP,58-193189,A is common. That is, they are the back degeneration method which uses a silylation reagent for \*\* polyvinyl alcohol or polyvinyl acetate, and introduces silicon, or the approach of copolymerizing and saponifying \*\* vinyl ester and a silicon content olefin monomer. Anyway, it is a rate as residue of a silicon content monomer, and 0.01-10-mol % is 0.1-2.5-mol % desirable especially preferably. Moreover, whenever [ saponification / 70-100 mol% of ] is desirable. polymerization degree — 3000-3000 — it is 600-3000 preferably.

[0012] About loadings with the glyoxal which is the curing agent of the silicon denaturation polyvinyl alcohol used for a protective layer, to the silicon denaturation polyvinyl alcohol 100 weight section, it is the range below 50 weight sections more than 3 weight sections, and 30 weight sections are preferably used from 10 weight sections. Furthermore, epichlorohydrin is the range below [ 3 weight sections to ] 50 weight sections to the silicon denaturation polyvinyl alcohol 100 weight section, and is 25 weight sections from 5 weight sections preferably. In addition, each above-mentioned loadings are a pure part weight ratio which contains neither water nor a solvent.

[0013] Moreover, for the purposes, such as performance-traverse amelioration, and note nature grant, seal nature grant, an inorganic or organic pigment may be added to a protective layer, and inorganic pigments, such as clay soil, talc, a kaolin, a baking kaolin, a calcium carbonate, an aluminum hydroxide, a magnesium carbonate, titanium oxide, a zinc oxide, and an amorphous silica, the organic pigment represented with a urea-resin are used for it as a pigment used. If the pigment in this case is made to contain five to 60% of the weight to the total solids of a protective layer, it is enough.

[0014] Furthermore, to a protective layer, waxes, such as defoaming agents, such as surfactants, such as dispersants, such as the various additives usually used for a thermal recording object, for example, sodium polyacrylate etc., and sodium dioctyl sulfosuccinate, and fatty-acid mono-GURISENAIDO, fluorescent dye and a color pigment, paraffin, oxidation paraffin, polyethylene, oxidation polyethylene, a sterol acid amide, and a caster wax, can be added.

[0015] The limitation according to rank does not have the base material used for this invention, for example, it can use suitably paper of fine quality, recycled paper, a piece glazed paper, oilproof paper, coat paper, art paper, cast coated paper, fine coated paper, a resin laminated paper, a polyolefine system synthetic paper, a synthetic-resin film, etc. Moreover, back layers, such as preparing the middle class who uses a pigment and a binder as a principal component between a base material and a sensible-heat coloring layer if needed and also curl adjustment, and antistatic treatment, can also be prepared.

[0016] The coloring component of the sensible-heat coloring layer on a base material can use what may be what kind of thing as long as it can form a record image with heating, for example, is depended on the reaction of a leuco color and the electronic receptiveness matter represented by the phenol nature matter, the thing to depend on the reaction of an imino compound and an isocyanate compound, the thing to depend on the reaction of long-chain-fatty-acid iron salt and a polyhydric phenol. The example of such combination is indicated by JP,54-118845,A etc. the amount of coating of a protective layer — the amount of desiccation solid content — 0.5 - 8 g/m<sup>2</sup> — desirable — the amount of coating of 1 - 4 g/m<sup>2</sup> and a sensible-heat coloring layer — 2 - 10 g/m<sup>2</sup> — it is 3 - 6 g/m<sup>2</sup> preferably.

[0017] The coating of the protective layer <stability test of a coating> Obtained was put for three days, and separation of a coating was observed. About a valuation basis, it is the following.

O : with no separation.

x: Those with separation.

[0018] The <\*\*\*\*\* blocking examining method> After KYUA [ the acquired thermal recording object ] under 40-degree-C30% of environment for 24 hours, it examined by printing by the canon handy terminal printer HT 9000. One drop of waterdrop was hung down to the recording surface of the thermal recording object after record, it was made 2 chip boxes so that a recording surface might become inside, and the load of 100 g/cm<sup>2</sup> was applied on the record object which trickled waterdrop, it was left under 20-degree-C65%RH for 24 hours, the recording surface was removed after that, and blocking was evaluated. About the valuation basis, it got with following one and \*\* (ed).

O : — blocking-less x: — blocking arises, a part of record layer is torn, and difficulty xx: blocking exfoliates [ decipherment of record ] from paper in size [0019] <Wet love trial> After KYUA [ the acquired thermal recording object ] under 40-degree-C30% of environment for 24 hours, one drop of waterdrop was hung down, it went five times with the finger, and the water resisting property of a paint film was evaluated.

O : a paint film is not taken.

\*\* : It is taken slightly.

x: A paint film is taken.

Although an example is given and this invention is explained in full detail more concretely hereafter, this invention is not limited to these.

[0020]

[Example]

<Example 1> <adjustment of sensible-heat coating liquid> A liquid: 3-dibutylamino-6-methyl-7-anilino fluoran Ten weight sections poly vinyl alcohol : 12% water solution 26.7 weight sections polystyrene acrylic-acid ammonium : 20% water solution The 1.6 weight section Water The 21.3 weight sections B liquid : [ 4-hydroxy-4'-isopropoxy diphenylsulfone ] 30 weight sections di(p-methylbenzyl) oxalate 30 weight section poly vinyl alcohol: 12% water solution 60 weight section polystyrene acrylic-acid ammonium: 20% water solution The 3.6 weight sections Water 78 weight sections [0021] About A liquid, it is mean particle diameter (the median size for which it asked with Horiba laser diffraction / dispersion type grain-size measuring device [LA910] is said.) with a Sand grinder. It is below the same. 0.5 micrometers or less were distributed until mean particle diameter was set to 0.8 micrometers about B liquid. A liquid adjusted above: Mixed churning of the 83.3 weight sections and the water 21.3 weight section was carried out for the 59.6 weight sections, the B liquid:201.6 weight section, and 12% of polyvinyl alcohol, and heat coating liquid was produced. By the test bar coating machine, it applied and dried and coating of the obtained sensible-heat coating liquid was carried out so that the amount of coating after an air dried might become 5 g/m<sup>2</sup> to the paper of fine quality of U.S. tsubo 50 g/m<sup>2</sup>, and the heat-sensitive recording layer was formed.

[0022] <Formation of a protective layer> On the obtained heat-sensitive recording layer, it is 12% water solution of silicon denaturation poly vinyl alcohol (R-1130: Kuraray make), the 350 weight sections, and a pigment. Spreading desiccation of the protective layer coating liquid which mixed the silica (Ms. KASHIRU -527: Mizusawa Industrial Chemicals make) 20 section, the 30% zinc stearate dispersion-liquid (hide phosphorus D-523: product made from Chukyo fats and oils) 33.3 weight section, the glyoxal (40% water solution) 25 weight section, the 12.5% water-solution 40 weight section of epichlorohydrin (WS-570: made in Japan

PMC), and the water 300 weight section, and was agitated was carried out by the test bar coating machine so that it might become 3 g/m<sup>2</sup>, and the protective layer was formed. Gloss calender processing was performed and the thermal recording object was acquired so that the surface Beck smoothness might become about 500 seconds after an appropriate time.

[0023] In formation of the protective layer of the <example 1 of comparison> example 1, the thermal recording object was acquired like the example 1 except having not used epichlorohydrin.

[0024] In formation of the protective layer of the <example 2 of comparison> example 1, the thermal recording object was acquired for epichlorohydrin like the example 1 not using glyoxal except \*\*\*\* for 80 weight sections.

[0025] In formation of the protective layer of the <example 3 of comparison> example 1, it replaced with glyoxal and the thermal recording object was acquired for 80% water solution (SUMIRE gap gin 613: Sumitomo Chemical make) of a melamine/formaldehyde like the example 1 except \*\*\*\* for the 12.5 weight sections.

[0026] In formation of the protective layer of the <example 4 of comparison> example 1, it replaced with glyoxal and the thermal recording object was acquired for 50% water solution (SUMIRE gap gin 636: Sumitomo Chemical make) of polyamide polyurea resin like the example 1 except \*\*\*\* for 20 weight sections.

[0027]

試験例	水濡れ ブロッッキング試験	ウェットラブ試験	塗料の安定性
実施例 1	○	○	○
比較例 1	○	△	×
比較例 2	×	○	○
比較例 3	×	△	×
比較例 4	×	△	×

[Table 1] : Evaluation result

[0028]

[Effect of the Invention] clear from Table 1 — as — the coating stability of a protective layer — high — the thermal recording object of this invention — a \*\*\*\*\* blocking property and a wet love property — it is the thermal recording object which was excellent in all.

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TECHNICAL FIELD

[Field of the Invention] This invention relates to amelioration of the \*\*\*\*\* blocking property of a protective layer established on the heat-sensitive recording layer in more detail about the thermal recording object which can record an image by thermal recording, a wet love property, and the stability of a protective layer coating.

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## PRIOR ART

[Description of the Prior Art] By having the sensible-heat coloring layer formed on the base material generally, and heating a sensible-heat coloring layer with a heat head, a heat stylus, laser light, etc., a thermal recording object makes the color coupler in a sensible-heat coloring layer react in an instant, forms a record image, and is widely known by JP,43-4160,B, JP,45-14039,B, etc. from the former.

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[0004] On the other hand, the conventional thermal recording ingredient has the fault which a record image fades or the natural complexion section colors by contacting organic solvents, such as fats and oils, such as plasticizers and salad oil, such as phthalic-acid diester represented by the dibutyl phthalate ester contained in a vinyl chloride case, and an aliphatic series dibasic acid ester, trialkyl phosphate, and a hand cream, or ethyl alcohol, and toluene, etc. In order to conquer such a fault, preparing a protective layer on a sensible-heat coloring layer from the former is performed, and water soluble polymers, such as polyvinyl alcohol and starch, etc. are used as a principal component as a component which constitutes this protective layer.

[0005] For this reason, when using the thermal recording object which moreover has a protective layer by rainy weather outdoors, if it contacts immediately after the thermal recording objects after record are damp in water, a thermal recording side, its rear face, or thermal recording sides will paste up. Fault, such as producing blocking and producing the poor feeding of the recording paper as a result, when a thermographic recording paper exfoliates and produces the problem that the recorded information cannot be read from paper, in being the worst, the end and, or waterdrop falls to the side face of winding before record and a sensible-heat side and its rear face paste up with waterdrop, has occurred.

[0006] Using together such a water soluble polymer and the cross linking agent which reacts as an approach of making it giving a water resisting property to the protective layer of a thermal recording object to solve this is performed. However, when heat energy which produces crosslinking reaction sufficient in the case of formation of a protective layer not being made giving, and a reactant high cross linking agent are used, crosslinking reaction arises in coating liquid, the viscosity of coating liquid increases remarkably, and there is a problem of coating becoming impossible etc.

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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

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## MEANS

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, this invention adopts the following configurations. That is, this invention is a thermal recording object characterized by this protective layer using glyoxal and epichlorohydrin together as a curing agent further using silicon denaturation polyvinyl alcohol in the thermal recording object which has a base material, the sensible-heat coloring layer formed on this base material, and the protective layer formed on this sensible-heat coloring layer.

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## EXAMPLE

## [Example]

<Example 1> <adjustment of sensible-heat coating liquid> A liquid: 3-dibutylamino-6-methyl-7-anilino-fluoran Ten weight sections poly vinyl alcohol : 12% water solution 26.7 weight sections polystyrene acrylic-acid ammonium : 20% water solution The 1.6 weight section Water The 21.3 weight sections B liquid : [ 4-hydroxy-4'-isopropoxy diphenylsulfone ] 30 weight sections di(p-methylbenzyl) oxalate 30 weight section poly vinyl alcohol: 12% water solution 60 weight section polystyrene acrylic-acid ammonium: 20% water solution The 3.6 weight sections Water 78 weight sections [0021] About A liquid, it is mean particle diameter (the median size for which it asked with Horiba laser diffraction / dispersion type grain-size measuring device [LA910] is said.) with a Sand grinder. It is below the same. 0.5 micrometers or less were distributed until mean particle diameter was set to 0.8 micrometers about B liquid. A liquid adjusted above: Mixed churning of the 83.3 weight sections and the water 21.3 weight section was carried out for the 59.6 weight sections, the B liquid: 201.6 weight section, and 12% of polyvinyl alcohol, and heat coating liquid was produced. By the test bar coating machine, it applied and dried and coating of the obtained sensible-heat coating liquid was carried out so that the amount of coating after an air dried might become 5 g/m<sup>2</sup> to the paper of fine quality of U.S. tsubo 50 g/m<sup>2</sup>, and the heat-sensitive recording layer was formed.

[0022] <Formation of a protective layer> On the obtained heat-sensitive recording layer, it is 12% water solution of silicon denaturation poly vinyl alcohol (R-1130: Kuraray make), the 350 weight sections, and a pigment. Spreading desiccation of the protective layer coating liquid which mixed the silica (Ms. KASHIRU -527: Mizusawa Industrial Chemicals make) 20 section, the 30% zinc stearate dispersion-liquid (hide phosphorus D-523: product made from Chukyo fats and oils) 33.3 weight section, the glyoxal (40% water solution) 25 weight section, the 12.5% water-solution 40 weight section of epichlorohydrin (WS-570: made in Japan PMC), and the water 300 weight section, and was agitated was carried out by the test bar coating machine so that it might become 3 g/m<sup>2</sup>, and the protective layer was formed. Gloss calender processing was performed and the thermal recording object was acquired so that the surface Beck smoothness might become about 500 seconds after an appropriate time.

[0023] In formation of the protective layer of the <example 1 of comparison> example 1, the thermal recording object was acquired like the example 1 except having not used epichlorohydrin.

[0024] In formation of the protective layer of the <example 2 of comparison> example 1, the thermal recording object was acquired for epichlorohydrin like the example 1 not using glyoxal except \*\*\*\* for 80 weight sections.

[0025] In formation of the protective layer of the <example 3 of comparison> example 1, it replaced with glyoxal and the thermal recording object was acquired for 80% water solution (SUMIRE gap gin 613: Sumitomo Chemical make) of a melamine/formaldehyde like the example 1 except \*\*\*\* for the 12.5 weight sections.

[0026] In formation of the protective layer of the <example 4 of comparison> example 1, it replaced with glyoxal and the thermal recording object was acquired for 50% water solution (SUMIRE gap gin 636: Sumitomo Chemical make) of polyamide polyurea resin like the example 1 except \*\*\*\* for 20 weight sections.

[0027]

試験例	水濡れ ブローキング試験	ウェットラフ試験	塗料の安定性
実施例 1	○	○	○
比較例 1	○	△	×
比較例 2	×	○	○
比較例 3	×	△	×
比較例 4	×	△	×

[Table 1] : Evaluation result

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(54) 【発明の名称】 感熱記録体

(57) 【要約】

【課題】 保護層の塗料安定性が高く、品質面では雨天の屋外で使用しても水濡れブロッキング等の問題が生じなく、耐水性に優れた感熱記録体を提供することを課題とする。

【解決手段】 支持体と、該支持体上に形成した感熱発色層と、該感熱発色層上に形成した保護層とを有する感熱記録体において、該保護層が珪素変性ポリビニルアルコールを用い、更に硬化剤としてグリオキサールおよびエピクロルヒドリンを併用することを特徴とする感熱記録体。

## 【特許請求の範囲】

【請求項 1】 支持体と、該支持体上に形成した感熱発色層と、該感熱発色層上に形成した保護層とを有する感熱記録体において、該保護層が珪素変性ポリビニルアルコールを用い、更に硬化剤としてグリオキザールおよびエピクロルヒドリンを併用することを特徴とする感熱記録体。

## 【発明の詳細な説明】

## 【 0 0 0 1 】

【発明の属する技術分野】 本発明は感熱記録方式によって画像を記録し得る感熱記録体に関し、更に詳しくは感熱記録層上に設けた保護層の水濡れブロッキング特性、ウェットラップ特性および保護層塗料の安定性の改良に関するものである。

## 【 0 0 0 2 】

【従来の技術】 感熱記録体は、一般に、支持体上に形成した感熱発色層を有し、感熱発色層を熱ヘッド、熱ペン、レーザー光等で加熱することにより、感熱発色層中の発色剤を瞬時に反応させ、記録画像を形成するものであり、例えば、特公昭 4 3 - 4 1 6 0 号公報や特公昭 4 5 - 1 4 0 3 9 号公報等により、従来から広く知られているものである。

【 0 0 0 3 】 これらの感熱記録体は、比較的簡単な装置によって記録画像を形成することができ、しかもメンテナンスが容易であり、また記録時の騒音も少ない等の利点を有することから、例えば計測用レコーダー、ファクシミリ、コンピューター等の端末用プリンタ、POS用プリンタ、自動券売機、バーコードラベルプリンタ等の広範囲の分野に応用されている。特に近年においては、各種チケット用、レシート用、銀行のATM用、ガスや電気の検針用などにも感熱記録体の用途が拡大してきており、このため、感熱記録体に対して従来では問題なっていなかったような厳しい特性が要求され始めている。即ち、感熱記録体に要求される特性は、耐候性や耐薬品性などにより、記録画像の退色や地肌かぶり等にたいする耐性を有することは勿論のこと、ガスや電気の検針用などの用途においては、屋外でしかも雨天で使用する

ことがあり、水に対する耐性も要求される。

【 0 0 0 4 】 一方従来の感熱記録材料は塩化ビニルケース中に含まれるフタル酸ジブチルエステルに代表されるフタル酸ジエステルや脂肪族二塩基酸エステル、リン酸トリエステルなどの可塑剤やサラダ油やハンドクリーム等の油脂類、またはエチルアルコールやトルエンなどの有機溶剤等に接触することにより記録画像の退色したり、地肌部が発色したりする欠点を有する。このような欠点を克服するために、従来から感熱発色層上に保護層を設けることが行われてきており、この保護層を構成する成分としてはポリビニルアルコールや澱粉などの水溶性高分子などが主成分として用いられている。

【 0 0 0 5 】 このため、屋外でしかも雨天で保護層のあ

る感熱記録体を使用する場合、記録後の感熱記録体同士が水に濡れた直後に接触すると感熱記録面とその裏面または感熱記録面同士が接着してしまい、最悪の場合には感熱記録紙が紙層から剥離し、記録された情報が読み取れないという問題を生じたり、記録前の巻取の側面に水滴が落ちて感熱面とその裏面が水滴で接着することによりブロッキングを生じ、結果的に記録紙の送り不良を生じるなどの不具合が起きている。

【 0 0 0 6 】 これを解決するには感熱記録体の保護層に耐水性を付与させる方法として、このような水溶性高分子と反応する架橋剤を併用することが行われている。しかしながら、保護層の形成の際に十分な架橋反応を生じようような熱エネルギーを付与させることができないこと、および反応性の高い架橋剤を使用すると塗液中で架橋反応が生じ塗液の粘度が著しく増大し塗工ができなくなるなどの問題がある。

【 0 0 0 7 】 このような問題を解決するために、水溶性高分子に反応性を高める官能基を導入することが提案されている。例えば特開昭 5 6 - 1 2 6 1 9 3 号公報、特開昭 5 9 - 1 0 6 9 9 5 号公報、特開昭 5 9 - 1 6 9 8 8 5 号公報、特開昭 6 2 - 2 6 4 9 9 0 号公報等の提案がなされているがこれら変性ポリビニルを用いても水濡れブロッキング特性は不十分である。

【 0 0 0 8 】 珪素変性ポリビニルアルコールを保護層に用いることは特開昭 5 8 - 1 9 3 1 8 9 号公報で公知の技術であるが、単独で用いると耐水性は付与できない。これらの欠点を補う為に珪素変性ポリビニルアルコールにグリオキザールを用いることが特開平 0 4 - 2 3 2 0 9 1 号公報、特開平 0 5 - 1 8 5 7 1 8 号公報で開示されている。しかしグリオキザール単独では塗料の安定性が低く、ウェットラップ特性にも課題が残る。更に特開平 8 - 1 8 3 2 5 2 において保護層に珪素変性ポリビニルアルコールにキトサンとグリオキザールを混合することが提案されているが、この提案でも塗料の安定性が低く、得られた感熱記録体が黄変しやすい等の欠点を有している。

## 【 0 0 0 9 】

【発明が解決しようとする課題】 本発明は保護層の塗料安定性が高く、品質面では雨天の屋外で使用しても水濡れブロッキング等の問題が生じなく、耐水性に優れた感熱記録体を提供することを目的とする。

## 【 0 0 1 0 】

【課題を解決するための手段】 上記課題を解決するため、本発明は以下の構成を採用する。即ち、本発明は、支持体と、該支持体上に形成した感熱発色層と、該感熱発色層上に形成した保護層とを有する感熱記録体において、該保護層が珪素変性ポリビニルアルコールを用い、更に硬化剤としてグリオキザールおよびエピクロルヒドリンを併用することを特徴とする感熱記録体である。

## 【 0 0 1 1 】

【発明の実施の形態】本発明に使用する珪素変性ポリビニルアルコールとは、分子内に珪素を含むポリビニルアルコールであればなんでも良い。その製造方法としては、特開昭 5 8 - 1 9 3 1 8 9 に記載されている方法が一般的である。即ち、①ポリビニルアルコールもしくはポリ酢酸ビニルにシリル化剤を用いて珪素を導入する後変性法、

②ビニルエステルと珪素含有オレフィンモノマーを共重合してケン化する方法のいずれかである。

いずれにしても、珪素含有モノマーの残基としての割合で、0. 0 1 ~ 1 0 モル%が好ましく、特に好ましくは、0. 1 ~ 2. 5 モル%である。また、ケン化度は 7 0 ~ 1 0 0 モル%が好ましい。重合度は 3 0 0 0 ~ 3 0 0 0 0、好ましくは、6 0 0 ~ 3 0 0 0 である。

【0 0 1 2】保護層に用いられる珪素変性ポリビニルアルコールの硬化剤であるグリオキサールとの配合量については、珪素変性ポリビニルアルコール 1 0 0 重量部に対して 3 重量部以上 5 0 重量部以下の範囲で、好ましくは 1 0 重量部から 3 0 重量部が用いられる。更にエピクロロヒドリンは珪素変性ポリビニルアルコール 1 0 0 重量部に対し 3 重量部から 5 0 重量部以下の範囲で、好ましくは 5 重量部から 2 5 重量部である。なお、上記の配合量はいずれも、水や溶媒を含まない純分重量比である。

【0 0 1 3】また保護層には走行性改良や筆記性付与、捺印性付与等の目的の為、無機もしくは有機の顔料を添加してもよく、使用される顔料としてはケイソー土、タルク、カオリン、焼成カオリン、炭酸カルシウム、水酸化アルミニウム、炭酸マグネシウム、酸化チタン、酸化亜鉛、非晶性シリカ等の無機顔料、および尿素樹脂で代表される有機顔料等が用いられる。この場合の顔料は保護層の全固形分に対して 5 ~ 6 0 重量%含有させれば充分である。

【0 0 1 4】更に、保護層には通常感熱記録体に用いられる各種添加剤、例えば、ポリアクリル酸ナトリウム等の分散剤、ジオクチルスルホコハク酸ナトリウム等の界面活性剤、脂肪酸モノグリセナイド等の消泡剤、蛍光染料や着色顔料、パラフィン、酸化パラフィン、ポリエチレン、酸化ポリエチレン、ステリン酸アミド、カスターワックス等のワックス類等も添加することができる。

【0 0 1 5】本発明に用いられる支持体は格別の限定は無く、例えば上質紙、再生紙、片艶紙、耐油紙、コート紙、アート紙、キャストコート紙、微塗工紙、樹脂ラミネート紙、ポリオレフィン系合成紙、合成樹脂フィルム等を適宜使用できる。また、必要に応じて、支持体と感

A 液：

3 - ジブチルアミノ - 6 - メチル - 7 - アニノフルオラン	1 0 重量部
ポリビニルアルコール：1 2 % 水溶液	2 6 . 7 重量部
ポリスチレンアクリル酸アンモニウム：2 0 % 水溶液	1 . 6 重量部
水	2 1 . 3 重量部

熱発色層の間に顔料、バインダーを主成分とする中間層を設けること、更にカール調整や帯電防止処理等のバック層を設けることもできる。

【0 0 1 6】支持体上の感熱発色層の発色成分は、加熱によって記録画像を形成し得るものであればいかなるものであっても良く、例えばロイコ染料とフェノール性物質に代表される電子受容性物質との反応によるもの、イミノ化合物とイソシアナート化合物との反応によるもの、長鎖脂肪酸鉄塩と多価フェノールとの反応によるもの等を利用し得る。これらの組み合わせの具体例は、例えば特開昭 5 4 - 1 1 8 8 4 5 号公報などに記載されている。保護層の塗工量は、乾燥固形分量で 0. 5 ~ 8 g / m<sup>2</sup>、好ましくは 1 ~ 4 g / m<sup>2</sup>、感熱発色層の塗工量は 2 ~ 1 0 g / m<sup>2</sup>、好ましくは 3 ~ 6 g / m<sup>2</sup> である。

【0 0 1 7】<塗料の安定性試験>得られた保護層の塗料を 3 日間静置し、塗料の分離を観察した。評価基準については下記。

○：分離無し。

×：分離あり。

【0 0 1 8】<水濡れブロッキング試験法>得られた感熱記録体を 4 0 ° C 3 0 % の環境下で 2 4 時間キュアした後、キャノンハンディーターミナルプリンタ H T 9 0 0 0 で印字を行い試験を行った。記録後の感熱記録体の記録面に水滴を 1 滴垂らし、記録面が内側になるように 2 つ折りにし、水滴を滴下した記録体の上に 1 0 0 g / c m<sup>2</sup> の荷重をかけ 2 0 ° C 6 5 % R H 下で 2 4 時間放置し、その後記録面を剥しブロッキングを評価を行った。評価基準については下記のとうりとした。

○：ブロッキング無し

×：ブロッキングが生じ、記録層の一部が破れ記録の判読が困難

××：ブロッキングが大で、紙層から剥離

【0 0 1 9】<ウェットラップ試験>得られた感熱記録体を 4 0 ° C 3 0 % の環境下で 2 4 時間キュアした後、水滴を 1 滴垂らし、指で 5 往復し塗膜の耐水性を評価を行った。

○：塗膜が取られない。

△：僅かに取られる。

×：塗膜が取られる。

以下、実施例を挙げて本発明をより具体的に詳述するが、本発明はこれらに限定されるものではない。

【0 0 2 0】

【実施例】

<実施例 1>

<感熱塗液の調整>

## B 液：

4-ヒドロキシ-4'-イソプロポキシジフェニルスルホン	30 重量部
シュウ酸ジ (p-メチルベンジル)	30 重量部
ポリビニルアルコール：12%水溶液	60 重量部
ポリスチレンアクリル酸アンモニウム：20%水溶液	3.6 重量部
水	78 重量部

【0021】A液についてはサンドグラインダーで平均粒子径（堀場製作所製レーザー回折／散乱式粒度測定装置 [LA910] で求めたメジアン径を言う。以下同じ。）が  $0.5\mu\text{m}$  以下に、B液については平均粒子径が  $0.8\mu\text{m}$  になるまで分散させた。上記で調整したA液：59.6重量部、B液：201.6重量部および12%のポリビニルアルコールを83.3重量部、水21.3重量部を混合攪拌し、熱塗液を作製した。得られた感熱塗液を米坪  $50\text{g}/\text{m}^2$  の上質紙に風乾後の塗工量が  $5\text{g}/\text{m}^2$  になるようテストバーコーターで塗布、乾燥し塗工し、感熱記録層を形成した。

【0022】＜保護層の形成＞得られた感熱記録層の上に、珪素変性ポリビニルアルコール（R-1130：クラレ製）の12%水溶液、350重量部、顔料としてシリカ（ミズカシル-527：水澤化学工業製）20部、30%ステアリン酸亜鉛分散液（ハイドリンD-523：中京油脂製）33.3重量部、グリオキザール（40%水溶液）25重量部、エピクロルヒドリン（WS-570：日本PMC製）の12.5%水溶液40重量部および水300重量部を混合、攪拌した保護層塗工液を  $3\text{g}/\text{m}^2$  になるように、テストバーコーターで塗布乾燥し保護層を形成した。しかる後に、表面のベック平滑

度が約500秒になるようにグロスクャレンダー処理を行い感熱記録体を得た。

【0023】＜比較例1＞実施例1の保護層の形成において、エピクロルヒドリンを用いなかった以外は実施例1と同様にして感熱記録体を得た。

【0024】＜比較例2＞実施例1の保護層の形成において、グリオキザールを用いなくエピクロルヒドリンを80重量部用いた以外は実施例1と同様にして感熱記録体を得た。

【0025】＜比較例3＞実施例1の保護層の形成において、グリオキザールに代えてメラミン／ホルムアルデヒドの80%水溶液（スミレーズレジン613：住友化学製）を12.5重量部用いた以外は実施例1と同様にして感熱記録体を得た。

【0026】＜比較例4＞実施例1の保護層の形成において、グリオキザールに代えてポリアミドポリ尿素樹脂の50%水溶液（スミレーズレジン636：住友化学製）を20重量部用いた以外は実施例1と同様にして感熱記録体を得た。

【0027】

【表1】：評価結果

試験例	水濡れ ブロッキング試験	ウェットラフ試験	塗料の安定性
実施例 1	○	○	○
比較例 1	○	△	×
比較例 2	×	○	○
比較例 3	×	△	×
比較例 4	×	△	×

【0028】

【発明の効果】表1から明らかなように、保護層の塗料安定性が高く、本発明の感熱記録体は水濡れブロッキン

グ特性、ウェットラフ特性いずれも優れた感熱記録体である。



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